LIQUID FUELS FROM SYNGAS - PROGRESS REPORT

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INTRODUCTION

Revolutionary changes lie immediately ahead for manufacture and use of transportation fuels. What will be their composition, technology for their manufacture and economic impact? On what basis will decisions be made? Major new requirements for fuel composition and the time table for their adoption have been set by the Clean Air Act Ammendment of 1990. Fuel values have become strongly dependent on environmental performance criteria. It has slowly become realized that such criteria have changed economics of fuel values. Higher environmental performance values justifies higher prices. For instance, methyl-tertiary-butyl ether, MTBE, sells for 1.5 times the price of gasoline.

Fuels manufactured from synthesis gas (H_2, CO, CO_2) offer special opportunities based both on environmental (decrease in CO and O_3) and energy performance (high octane or cetane ratings). Further, syngas can be made not only from abundant coal and gas, but also from biomass. Biomass has the advantage of providing a renewable energy source. It also has the special advantage of avoiding net production of CO_2 and so helps to minimize the greenhouse effect.

SOCIETAL FACTORS INFLUENCING FUELS SELECTION

Several recent events now shape the selection of fuels and, consequently, R & D relative to their manufacture and use. Pollution assessments EPA has determined that >100 city areas have not attained a sufficiently low level of CO or O_3 in their air deemed essential for health. This was influential in passage of the Clean Air Act Amendment of 1990 which requires, among other things: 1992 Gasoline in 44 city areas in which winter fuels must contain 2.7% oxygen (equivalent to 15% MTBE or 8% EtOH), 1995 Gasoline must contain 2% oxygen in 9 city areas year round, 1998 Fleets of 10 or more vehicles in ozone non-compliance areas to have at least one vehicle capable of using alternative fuel. In an understatement the administration has said that "The CAAA's of 1990 were not intended to be an energy policy, but because of their major impact on the energy industry, they will have significant effect on energy use."

Reformulated Gasoline ARCO led the way by marketing a less polluting gasoline with at least 1% O (contains MTBE) lower benzene and lower vapor pressure. M 85 fuel, containing 85% methanol and 15% hydrocarbons, is increasingly marketed in California and elsewhere. Flexible Fuel Vehicles, FFV's, capable of using alcohol, gasoline, or mixtures, have been developed, tested extensively, and are near mass production. Exemption of federal tax for gasoline known as Gasohol, containing 10% agricultural ethanol (equivalent to 60 cents/gal ethanol), extended to ethyl-tertiary-butyl ether, ETBE. National Energy Strategy 1991 was issued by the U.S. Department of Energy. Increased oil production was stressed. No increase in CAFE was proposed. Increased support, incentives, and requirements were advocated for alternative fuels, particularly for renewable fuels.

NEAR TERM PROGRESS - HYDROCARBON FUELS

Several new or improved catalytic processes to provide fuel from syngas have been installed or are in an advanced development stage. Methanol-to-Gasoline The MTG process, developed by Mobil in partnership with DOE, has been in operation in New Zealand for six years. It supplies the equivalent of 1/3 of New Zealand's gasoline requirements. First, and fundamental to the concept for its installation, this plant meets the national policy of relative energy independence. Now privately owned

(25% by Mobil Oil continued) the investment debt has been paid. Gasoline is being exported to Japan, valuable there because of its high octane. Improvements in the MTG process have been made since its New Zealand installation in fixed-bed form. The TIGAS variation, developed by Topsoe (1), provides for plant savings by process integration. Alternatively, a fluid bed catalytic version of MTG, having improved economics (2), has been demonstrated on a semicommercial scale.

Slurry FT + ZSM 5 This concept consists of slurry phase FT followed by upgrading of the products over a ZSM 5 catalyst. Two modes of operation were established - a low wax and a high wax mode (3). The wax can be further upgraded to gasoline and diesel fuel. Excellent yields of high quality fuels were demonstrated, Table 1. Fixed Bed FT + Hydrocrack A problem with the usual FT process is the production of methane. The Shell Oil Company is pioneering the concept of carrying out syngas hydrogenation using a catalyst, possibly based on cobalt rather than iron, under conditions that result in a high degree of polymerization. When operated with an alpha (ASF relationship) of 0.9 or above, the reactor product consists of high molecular weight alkanes, Fig. 1 (4). Modern technology provides that the wax product can be efficiently hydrocracked to produce a kerosene and high quality diesel fuel. It is estimated that the energy efficiency of gas to product is 60%. A large plant in Malaysia is scheduled to come on stream in 1993.

Cobalt Catalysts Goodwin has pointed out (5) that a number of patents have been issued involving cobalt instead of iron for slurry FT, Table 2. It is proposed that the second metal functions by permitting reduction of the cobalt salt at a lower temperature, thereby providing a larger cobalt metal surface area and higher activity. The question of the difference between Fe and Co on removal of oxygen as H_2O or CO_2 is of considerable interest.

Slurry FT Using Landfill Gas for Syngas The Fuel Resources Development Company, a subsidiary of Public Service Company of Colorado, has built a small plant near Denver in which landfill methane is converted to syngas and then to hydrocarbon fuels using the slurry catalyst technique (6), pioneered by Koelbel in Germany (1). A Fe catalyst is used. Tests by Detroit Diesel Corp. (7) showed an excellent diesel fuel can be made, Table 3, which on combustion showed a surprisingly favorable particulate reduction. It was concluded that the presence of oxygenates contributed significantly to the particulate reduction. The fuel contained 12% oxygenates. This draws attention to the potential for oxygenates in diesel fuels.

A pilot plant trial of slurry FT is planned in 1992 at the Air Products pilot plant at La Porte, TX, inspired by the projected improved economics, discussed later.

NEAR TERM PROGRESS - OXY-FUELS

The initial rationale for use of oxygenates in fuels was based on their high octane properties. Now, the dominant benefit is regarded as environmental. It is believed that CO and O_3 pollution from automotive fuel combustion is lowered about 25% by their use. Also in their favor is the fact that they can be made from sources other than petroleum including biomass. Regulations arising from the Clean Air Act Amendments are powerful determinants. The remarkable growth of MTBE (8) dominates the changes in fuel composition and manufacture (now 6 MM gallon per day for MTBE vs. 300 for gasoline in USA) Fig. 2. Much of the technology for MTBE manufacture, Fig. 3, has long been known. One interesting technical innovation is the use of the alcohol + isobutylene to ether conversion catalyst as distillation column packing. This application helps overcome reaction equilibrium limitations and so enhances higher ether productivity.

The extensive growth in MTBE has now resulted on an impending shortage in isobutylene, generally obtained as a "by-product" from catalytic cracking. This has inspired research searching for cracking catalysts which produce larger amounts of suitable olefins. The shortage in isobutylene is being met by worldwide installation of plants for dehydrogenation of isobutane by processes licensed by United Catalysts (Houdry Catofin), Phillips Petroleum (Star), UOP, and Snamprogetti. It is of considerable interest that isobutylene can be manufactured from syngas. This involves first production of isobutanol, IBA, which is catalytically dehydrated.

The technology for hydrogenation of CO to <u>mixed alcohols</u> has been developed extensively. Product distributions from several processes offered commercially are shown in Table 4. It has been noted that in the Lurgi process 60% of the C_4 alcohols is isobutanol. One research report (9) claims 59% isobutanol from syngas using an optimized catalyst. The use of catalysts containing alkali, particularly cesium, increases isobutanol formation, Fig. 4 (10). A trial is planned in 1992 to test such a catalyst in slurry form in the Air Product's pilot plant in La Porte. It can be noted that mixed alcohols containing C_1, C_2, C_3 is not now well regarded. MTBE is considered to be much more fungible (ie compatible, trouble free). One important technological feature noted in Table 3 is the ability to recycle lower alcohols to produce higher alcohols. There is some evidence that C_2 and C_3 alcohols are so converted, but MeOH is converted back to syngas. However, even if the methanol is converted to syngas, this ultimately is transformed into higher alcohols. This is a distinct advantage over similar hydrocarbon synthesis where methane which is formed does not revert to syngas, but must go to a separate and costly reforming step.

A further consideration of <u>IBA as a fuel</u> is its potential as a competitor of MTBE. IBA has a good octane rating and lower vapor pressure, Table 5. IBA is highly hydrocarbon-soluble and so does not suffer disadvantages of lower alcohols for phase separation in the presence of water. Thus starting with IBA, is it better to use it as such or convert to MTBE? Starting with isobutylene, is it better to add H_2O or MeOH? It also should be mentioned that there are a number of other oxygenates which have potential markets. These include not only other ethers such as TAME, DME, diisopropyl ether, but also dimethyl carbonate and other oxygenates.

More economical <u>synthesis of methanol</u> has been developed by extensive research and pilot plant testing using a slurry catalyst system at Air Products pilot plat at La Porte with support of DOE. Extensive background practical engineering know-how information was established regarding fluid dynamics, catalyst stability, etc. Major improvements in through-put have been achieved by techniques such as more efficient gas distribution configurations. Decreased investment costs have been made possible by demonstration of simpler heat exchange equipment. Also a big step forward was catalyst systems which could catalyze shift as well as synthesis, thus providing the means of being able to use directly low H_2/CO ratio gas from modern gasifiers. Recently also, it has been demonstrated (11) that by coproduction of MeOH and dimethyl ether, DME, much higher CO conversion per pass is achieved since the same thermodynamic limitations do not apply. This provides for lower recycle costs and also potential for manufacture from DME.

It also should be noted that the Eastman plant which manufactures acetic anhydride from syngas from lignite also produces and markets methanol. It is certainly a convincing evidence of the economic viability that this plant has been expanded recently. It is claimed that the key for success is efficient integration of modern technology.

MID/LONGER TERM

A wide variety of novel syngas conversion catalysts have been investigated, testing novel concepts, particularly for synthesis of oxygenates. Technical progress reviewed in 1988 (1) included research ideas involving partial poisoning, metal dispersion control, melts, alloys, metals in zeolites, multimetals, sulfides, and biocatalysts. Only a few will be mentioned because of space limitations. Isobutanol synthesis has been referred to above. Catalysts derived from certain <u>rare earth/copper alloys</u>, such as $CeCu_2$, have been found to exhibit extraordinarily high catalytic activity for hydrogenation of CO to methanol (1). They are active at 100°C. Unfortunately, these catalysts are deactivated by low concentrations of CO_2. Possibly new methods of preparation or purification of syngas free from CO_2 can make these catalysts of practical interest.

<u>Dual function catalysts</u>, such as $Rh-MoO_x/Al_2O_3$, have been found to activate CO by Rh and hydrogen by MoO_x sites not inhibited by CO (I). The enhanced kinetics then provides highly active catalysts

and point the direction for future design of even more active catalysts for selective production of alcohols at low temperature.

There is a new interest in systems involving CO activation using base catalysts such as KOCH$_3$ (12). Methyl formate is the first formed which is subsequently hydrogenated to methanol by a catalyst such as copper chromite. CH$_3$OH $\rightarrow$ HCOOCH$_3$ + H$_2$ $\rightarrow$ 2CH$_3$OH. A limitation has been that such base catalyst are inactivated by H$_2$O or CO$_2$. New interest has been sparked by the report that there is a tolerance for low levels of H$_2$O and CO$_2$ by simultaneous use of both catalysts.

For the longer term, there is promise of progress from information developed by surface science and biocatalysis studies as well as new approaches such as use of artificial intelligence or computer graphics for catalyst design.

ECONOMICS

Because of thermodynamic limitations, the energy efficiency of indirect liquefaction is lower than for direct liquefaction of coal. It has been erroneously stated that, therefore, indirect is more costly than direct liquefaction. However, the cost of a synthetic fuel is much more dependent on plant investment costs than on raw materials costs. Manufacturing charges include not only costs directly attributable to operation of an expensive plant such as maintenance and insurance, but also necessary charges for profit and taxes. For a generalized synfuels from coal plant, (13) production cost, 10^6 Btu, is 3.21, made up of coal 1.42, operating costs 0.19, and capital charges of 1.60. Selling price required includes profit 1.42, taxes 1.42 equal to 6.05 (ca $36/bbl). As mentioned above, a further consideration of synfuel economics is the value placed on their environmental performance qualities.

Perhaps the most striking economic news is the estimates which have been made for use for the production of diesel and gasoline from syngas using of modern gasifiers coupled with slurry FT. The resulting increase in energy efficiency and decease in selling price is shown in Table 6 (14). The $42/bbl price for gasoline/diesel which makes slurry FT is as low or lower than direct liquefaction for the same products (not crude oil) made by direct liquefaction of coal.

It may be pertinent to notice the costs of subsidization for the Gasohol program in the USA (15). The federal tax benefit is 60 cents/gallon of alcohol used in Gasohol. In 1987 there were 55,400 barrels/day ethanol fuel sales corresponding to a subsidy of about $500,000,000 annually. There is an additional subsidy in the corn used to produce the ethanol.

ACKNOWLEDGEMENT

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TABLES

Table 1: Stages FT/ZSM 5/ Alkylation

Product	Yield, Wt		
	After FT	After ZSM 5	After Alkylation
C_1	7.5	7.7	7.7
$C_2 = /C_2$	1.6/3.0	1.1/3.1	1.1/3.1
$C_3 = /C_3$	8.0/2.2	4.0/5.1	0/5.1
$C_4 =$	6.6	4.4	0
iC_4/nC_4	0/2.0	7.8/4.3	(2.2)/4.3
$C_5 - C_{11}$	33.5	52.8	71.2*
C_{12+} (Liq)	27.8	1.7	1.7
Wax	8.0	8.0	8.0

* Octane Rating: Research 90, Motor 83

Table 2: Patented Co - Based FT Catalysts

Company	Typical Constituents			
	Primary	Secondary 1	Secondary 2	Support
Gulf	Co	Ru	Oxides	Alumina
Exxon	Co	Re/Ru	Oxides	Alumina
Shell	Co	w/wo noble metal	ZrO_2	Silica
Statoil	Co	Re	Oxides	Alumina

Table 3: Synthetic Diesel Fuel

	Composition, Wt. %
Sulfur	< 0.001
Aromatics	0
Paraffins	47
Olefins	41
Alcohols	6
Other Oxygenates	6
Cetane Index	62

Table 4: Composition of Fuel Alcohols From Syngas

Alcohol %	C_1	C_2	C_3	C_4	C_5	Other Oxygenates	Catalyst
MAS (SEHT)	69	3	4	13	9	2	K/Zn/Cr
Substifuel (IFP)	64	25	6	2	2.5	0.5	K/Cu/Co/Al
Octamix (Lurgi)	62	7	4	8	19	--	Alkali/Cu/Zn/Cr
HAS (DOW)	26*	48	14	3.5	0.5	8	$CoS/MoS_2/K$

* Methanol can be recycled to extinction, increasing ethanol

Table 5: Properties of Some Fuel Oxygenates

	Blending RVP	Blending Octane	BTU/Gallon 1000's	Production MMgpd
MTBE	8	110	109	6.1
ETBE	4	110	117	
TAME	2	103	112	
t-Butanol	9	100	101	
iso Butanol	5	102	95	
Gasoline		87	125	300

Table 6: Improvements in Indirect Liquefaction of Coal

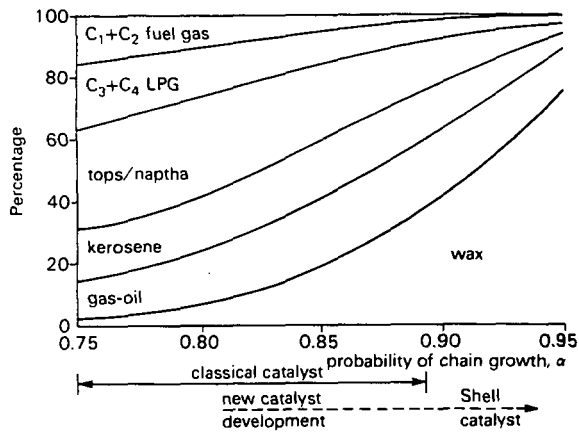| Processes	Lurgi + Arge FT	Shell + Arge FT	Shell + Slurry FT
Plant Output, Bpsd			
Alcohols	1,762	1,836	1,954
Propane	4,467	4,037	4,207
Butane	5,403	5,522	5,560
Gasoline	36,450	32,494	33,953
Diesel	35,419	39,617	37,828
Total	83,501	83,505	85,503
Energy Efficiency %	48	53	59
Required Selling Price, $/Bbl	55	48	42

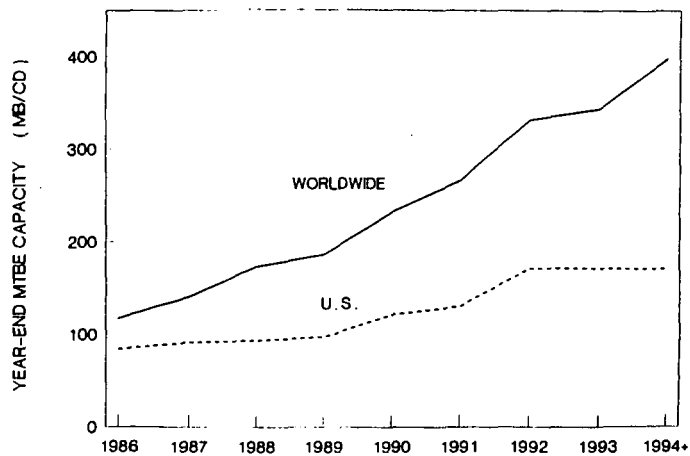Fig. 1 Product Distribution for Fischer Tropsch Synthesis
as a Function of Alpha

Fig. 2 U.S. and World Production Capacity of MTBE
Based on Announced Additions

iC₄H₉OH → iC_4H_9OH

$$\begin{array}{c}
& & iC_4H_9OH \\
& \nearrow^{1} & \searrow^{3} & & CH_3 \\
CO \\ H_2 & \xrightarrow{2} & CH_3OH + iC_4H_8 & \xrightarrow{6} & CH_3\overset{|}{\underset{|}{OC}}-CH_3 \\
& & \nearrow_{5} & & CH_3
\end{array}$$

$$nC_4H_{10} \xrightarrow{4} iC_4H_{10}$$

1	Cu-ZnO-Al₂O₃-Alkali	4	Pt-Cl-Al₂O₃
2	Cu-ZnO-Al₂O₃	5	Cr₂O₃-Al₂O₃
3	ACID	6	ACID RESIN

1 $Cu\text{-}ZnO\text{-}Al_2O_3\text{-}Alkali$ 4 $Pt\text{-}Cl\text{-}Al_2O_3$
2 $Cu\text{-}ZnO\text{-}Al_2O_3$ 5 $Cr_2O_3\text{-}Al_2O_3$
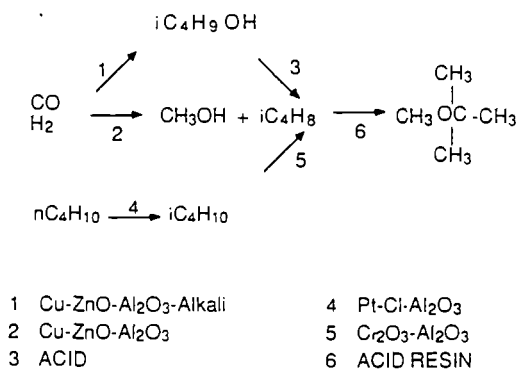3 ACID   6 ACID RESIN

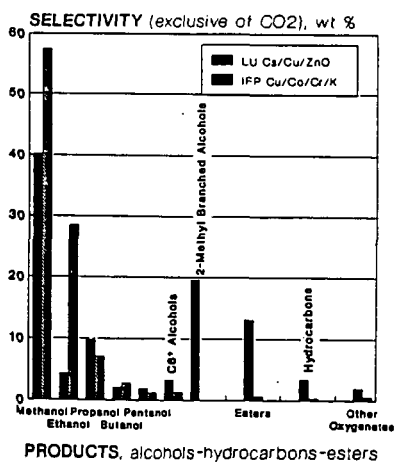Fig. 3 Reactions and Catalysts for MTBE Synthesis

Fig. 4 Synthesis of Alcohols Over Cs / Cu / ZnO
and Cu / Co / Cr / K Catalysts